



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> :	A1	(11) International Publication Number:	WO 00/01775
C09D 5/03		(43) International Publication Date:	13 January 2000 (13.01.00)

(21) International Application Number:	PCT/GB99/02109	(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
(22) International Filing Date:	2 July 1999 (02.07.99)	
(30) Priority Data:	9814519.6 3 July 1998 (03.07.98) GB	
(71) Applicant (for all designated States except US):	INTERNATIONAL COATINGS LIMITED [GB/GB]; Oriel House, 16 Connaught Place, P.O. Box 20980, London W2 2ZB (GB).	
(72) Inventors; and		
(75) Inventors/Applicants (for US only):	RING, John [GB/GB]; 26 Meadowvale, Darras Hall, Ponteland, Newcastle-upon-Tyne NE20 9NF (GB). CRAPPER, Gareth, Dale [GB/GB]; 4 Union Street, North Shields, Tyne & Wear NE30 1NL (GB). KITTLE, Kevin, Jeffrey [GB/GB]; 19 Denwick Close, Chester-le-Street, Co. Durham DH2 3TL (GB).	
(74) Agents:	COULSON, Antony, John et al.; Abel & Imray, 20 Red Lion Street, London WC1R 4PQ (GB).	

(54) Title: POWDER COATING COMPOSITIONS

## (57) Abstract

Powder coating compositions incorporate, by dry blending, a wax-coated silica additive in finely divided form. Further additives which may be incorporated by dry blending are aluminium oxide and/or aluminium hydroxide. The compositions offer advantages, for example, in terms of fluidity and in terms of improved first-time deposition of fine particles.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

POWDER COATING COMPOSITIONS

This invention relates to powder coating compositions and to their use.

Powder coatings form a rapidly growing sector of the coatings market. Powder coatings are solid compositions which are generally applied by an electrostatic spray process in which the powder coating particles are electrostatically charged by the spray gun and the substrate is earthed. Charging of the powder in the spray gun is effected by means of an applied voltage or by the use of friction (tribo-charging). Conversion of the adherent particles into a continuous coating (including, where appropriate, curing of the applied composition) may be effected by heat treatment and/or by radiant energy, notably infra-red, ultra-violet or electron beam radiation. The powder coating particles which do not adhere to the substrate can be recovered for re-use so that powder coatings are economical in use of ingredients. Also, powder coating compositions are generally free of added solvents and, in particular, do not use organic solvents and are accordingly non-polluting.

Powder coating compositions generally comprise a solid film-forming resin, usually with one or more colouring agents such as pigments, and optionally also contain one or more performance additives. They are usually thermosetting, incorporating, for example, a film-forming polymer and a corresponding curing agent (which may itself be another film-forming polymer), but thermoplastic systems (based, for example, on polyamides) can in principle be used instead. Powder coating compositions are generally prepared by intimately mixing the ingredients (including colouring agents and performance additives) for example in an extruder, at a temperature above the softening point of the film-forming

polymer(s) but below a temperature at which significant pre-reaction would occur. The extrudate is usually rolled into a flat sheet and comminuted, for example by grinding, to the desired particle size.

5 In the case of powder coating compositions which are to be applied by electrostatic spraying, film thicknesses of 40 microns to over 100 microns are common. The particle size distribution of the composition will normally be in the range of from 0 to 120 microns, with a mean  
10 particle size in the range of from 15 to 75 microns, preferably 25 to 50 microns, more especially 20 to 45 microns.

Powder coating compositions of such conventional particle size are widely used in the industry. Some of  
15 the known drawbacks encountered with these materials are associated with the application characteristics of the powders. The ease with which the powder fluidises and is transported through the application equipment affects the uniformity of film weight distribution across the  
20 substrate and as a consequence the amount of powder needed to achieve "on average" the desired film thickness. With these conventional powder coatings the first-time deposition of the fine particles (especially powder particles of 10 microns diameter or less) is  
25 inefficient leading to an accumulation of fine particles (fines) in the over-sprayed material. In many instances, the over-sprayed material is collected and recycled for re-use. In such systems, as the powder application process continues, the percentage of fine powder  
30 particles in the recycled powder increases and the cohesive behaviour of the fines starts to influence the properties of the recycled powder. The major effect is that the powder loses fluidity and this causes increasing difficulties in transporting the powder through the  
35 recycle system and back to the spray gun.

Another well-known problem with using powder coating compositions of such conventional particle size

- 3 -

distribution is the difficulty of applying thin film coatings of, say, 30 microns or less, for which there is an increasing demand in certain sectors of the powder coating market, whilst achieving a uniform opacity and an aesthetically pleasing appearance, particularly in a gloss white coating. Using compositions of conventional particle size distribution, the achievement of such results is possible only within a restricted range of powder chemistries, with the best performance generally being obtained with polyurethane powders using blocked isocyanates. To achieve coatings of less than 20 microns with a uniform opacity and an aesthetically pleasing appearance with compositions of conventional particle size distribution is very difficult if not impossible.

The problems encountered ("orange-peel" imperfections, etc.) are considered to be attributable to the relatively large size of the majority of the particles in powder coating compositions of conventional particle size distribution.

In addition to the increasing demands within the powder coatings market itself, it has also been recognised that the inability of powder coatings reliably and routinely to achieve film thicknesses of 30 microns or less with aesthetically pleasing appearance is one of the factors that has inhibited further substitution of solvent-based "wet" paints by powder coatings.

It has been proposed that the problems of achieving satisfactory thin film powder coatings can in principle be alleviated with the use of powder coating compositions of a finer particle size. There are problems, however, in the fluidisation, handling and application of relatively small particles, especially particles which are 10 microns in diameter or less. Such problems become more pronounced as the proportion of fine particles increases, and powder coating compositions have conventionally been manufactured so as to comprise not

more than 10% by volume of particles which are 10 microns in diameter or less.

WO 94/11446 discloses powder coating compositions which incorporate, by dry-blending, various combinations 5 of two or more additives, the preferred combination being aluminium oxide with aluminium hydroxide. By using combinations of dry-blended additives in accordance with WO 94/11446, it is possible to alleviate the problems of fluidisation, handling and application of fine particles 10 (especially those of 10 micron diameter or less) as outlined above and also to alleviate other problems attributable to differential and premature electrostatic charging of the powder particles. WO 94/11446 is directed to powder coating compositions of which at 15 least 95% by volume has a particle size not exceeding 50 microns.

Although good results are achievable using the additive combinations disclosed in WO 94/11446, it has been found inter alia that the optimum blend of aluminium 20 oxide/aluminium hydroxide, in terms of the fluidity, transport and handling characteristics of the powder coating composition, tends to detract from the utility of the composition in tribostatic application processes. Attempts to compensate for that effect by increasing the 25 proportion of aluminium oxide in the additive combination tend to result in powder coating compositions having less good fluidity and transport properties.

EP-A-0 300 818 suggests that tribo-charging characteristics can be conferred on powder coating compositions 30 of conventional particle size distribution by the use of an additive which comprises one or both of aluminium oxide and/or hydroxide, which has been sheared (by high-speed shearing or milling) such that the additive resulting therefrom is a fine, essentially aggregate-free 35 powder which comprises at least 5% by weight of particles of maximum size 0.2 microns. According to EP-A-0 300 818, a preferred way of achieving the

specified particle size requirement is to add to the aluminium oxide/hydroxide, prior to shearing, a proportion of a fine particle extender of maximum particle size 0.2 microns. The preferred extender 5 disclosed in EP-A-0 300 818 is fumed silica, but it has been found that the inclusion of fumed silica tends to detract from the efficiency of an aluminium oxide/aluminium hydroxide additive (as proposed in WO 94/11446) in terms of fluidity and transport characteristics, so 10 that the optimum benefit of the additive combination in terms of those characteristics is not achieved.

The present invention provides a powder coating composition which incorporates, by dry blending, a wax-coated silica in finely-divided form.

15 The term "coating" as used herein in relation to silicas for use according to the invention includes impregnation of porous silica materials, and the expression "coated silica" is to be understood accordingly.

20 The term "silica" as used herein includes materials obtained by pyrogenic and, preferably, wet processes leading to precipitated silicas or silica gels, as well as, in principle, mixed metal-silicon oxides and naturally-occurring materials such as, for example, 25 diatomaceous earth. Silicas for use according to the invention will in general have an amorphous structure. The term "silica" includes silicic acid materials. Silicates also come into consideration.

A preferred material comprises micronised silica 30 gel.

The term "wax" as used herein includes:

- i) Natural animal waxes (for example, beeswax, lanolin);
- ii) Natural vegetable waxes (for example, carnauba wax);
- 35 iii) Natural petroleum waxes (for example, paraffin wax, microcrystalline wax);

iv) Synthetic waxes (for example, ethylenic polymers and polyol ether-esters).

Mineral waxes other than petroleum waxes may also 5 come into consideration.

An important group of waxes for use in accordance with the invention comprises esters of long-chain aliphatic alcohols (typically C<sub>16</sub> and above) with long-chain fatty acids (typically C<sub>16</sub> and above). Such esters 10 and acids are preferably straight-chain compounds, and may be saturated or unsaturated. Examples of acids which may be used include stearic acid, palmitic acid and oleic acid and mixtures of two or more thereof.

Waxes derived from long-chain aliphatic compounds as 15 described above may include hydrocarbons.

In addition to esters of the long-chain acids as described above there may be mentioned salts such as, for example, aluminium stearate.

Preferred wax materials for use in accordance with 20 the invention are materials which have good compatibility with the polymer component(s) of the powder coating composition, that is to say, materials which can be mixed homogeneously with the polymers without significant phase separation. It will be found that some wax 25 materials (for example, halogenated waxes) are in general not compatible in this sense with the powder coating polymer(s). The use of such materials would be expected to give rise to defects in the surface appearance of the finished applied coating, and is 30 accordingly not recommended.

Wax-coated silicas suitable for use in accordance with the invention include commercially available materials such as, for example, GASIL 937 ex Crosfield (a silica gel coated with microcrystalline paraffin wax) 35 and OK 607 ex Degussa (a similar material with a coating which also includes a short-chain [C<sub>6</sub>] saturated amine or alkyl ammonium component).

Coating of the silica material may be effected by methods known in the art, for example, by co-milling of the silica with a solid wax material, or by admixing the silica material with a wax material dissolved in a 5 suitable solvent which is then evaporated.

The amount of wax coated onto the silica may, for example, be in the range of from 2 to 10% by weight, based on the weight of the silica.

Further information concerning wax-coated silicas 10 which may be used in accordance with the invention may be found in U.S. Patent Specifications Nos. 3 607 337 and 3 816 154, and in WO 97/08250. In addition to wax-coated silica, a powder coating composition of the invention may incorporate, also by dry blending, aluminium oxide and/or 15 aluminium hydroxide, preferably aluminium oxide or aluminium oxide and aluminium hydroxide. Aluminium oxy-hydroxide may be used in addition to or instead of aluminium hydroxide. It is believed that any of the main structural types of these materials may be used, that is 20 to say:

$\alpha$	-	$\text{Al}_2\text{O}_3$	Corundum	
$\alpha$	-	$\text{AlO(OH)}$	Diaspore	
$\alpha$	-	$\text{Al(OH)}_3$	Bayerite	
$\gamma$	-	$\text{Al}_2\text{O}_3$		
25	$\gamma$	-	$\text{AlO(OH)}$	Boehmite
	$\gamma$	-	$\text{Al(OH)}_3$	Gibbsite

Preference may be given to  $\gamma$ -structural types.

The proportion of wax-coated silica incorporated in a powder coating composition of the invention may in 30 general be in the range of from 0.002 to 2.0% by weight, based on the total weight of the composition without the additive, advantageously from 0.02 to 1.5% by weight and preferably from 0.04 to 1.0% by weight, more especially at least 0.2% by weight, especially 0.3 to 0.7% by 35 weight, for example, 0.3 to 0.5% by weight.

The total content of the wax-coated silica

additive(s) and, if present, the other dry-blended additive(s) specified above, incorporated in a powder coating composition of the invention, may in general be in the range of from 0.1 to 5% by weight, based on the 5 total weight of the composition without the additive(s), advantageously 0.1 to 2% by weight, preferably at least 0.2% by weight, especially 0.2 to 1.5% by weight, and more especially 0.3 to 1% by weight.

In the case in which the powder coating composition 10 includes dry-blended additives comprising wax-coated silica and aluminium oxide, the relative proportions of silica to aluminium oxide may in general be in the range of from 99:1 to 1:99, advantageously from 80:20 to 20:80, and preferably 70:30 to 30:70, for example 50:50.

15 In the case in which the dry-blended additives comprise wax-coated silica and aluminium hydroxide, the relative proportions of silica to the aluminium hydroxide may in general be from 99:1 to 30:70, advantageously from 90:10 to 40:60, preferably from 80:20 to 50:50, for 20 example 65:35.

In the case in which the dry-blended additives comprise wax-coated silica, aluminium oxide and aluminium hydroxide, the relative proportions of the additives may in general be as follows:

25	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Al}(\text{OH})_3$
	—	—	—
advantageously	1 to 98%	1 to 98%	1 to 70%
preferably	5 to 50%	10 to 90%	1 to 60%
	10 to 30%	20 to 85%	1 to 55%

30 In preferred forms of composition according to the invention, the dry-blended additive(s) consist solely of wax-coated silica or, as the case may be, wax-coated silica with aluminium oxide and/or aluminium hydroxide.

As a generality, the greater the proportion of 35 particles of below 10 microns in diameter in the composition, the higher the proportion of dry-blended additive(s) that is preferred for use in accordance with

- 9 -

the invention. This relationship may be illustrated by the following table, which also includes (as independent variables) typical ranges for  $d(v)_{50}$  and  $d(v)_{99}$  for the compositions:

	% by volume below 10 microns	$d(v)_{50}$	$d(v)_{99}$	% additive(s) by weight
--	---------------------------------	-------------	-------------	----------------------------

	< 18%	18-22 microns	52-58 microns	0.6 - 1.0
	< 12%	25-30	60-80	0.4 - 0.6
10	< 8%	30-40	80-120	0.2 - 0.4

Advantageously, in the case in which there is more than one dry-blended additive, the additives are pre-mixed, preferably intimately and homogeneously by a high-shear technique, before being incorporated in the powder coating composition. In the case of three dry-blended additives, all three may be blended together in a single mixing operation, or any two of the three may first be blended together with the third additive being mixed in afterwards.

Although any additive or mixed sub-combination of additives may in principle be incorporated separately in the powder coating composition, pre-mixing of additives is generally preferred.

The additive(s) of the invention may be incorporated in the powder coating composition by any available dry-blending method, for example:

- (a) injection at the mill, with the chip and additive(s) fed into the mill simultaneously;
- 30 (b) introduction at the stage of sieving after milling; and
- (c) post-production blending in a "tumbler" or other suitable mixing device.

The particle size of each dry-blended additive may be up to 5 microns, or even up to 10 microns in some cases. Preferably, however, the particle size is not greater than 2 microns, and is more especially not

- 10 -

greater than 1 micron. In general, the lower the thickness of the coating that is to be applied, the smaller the particle size of the additives. The preferred minimum additive particle size is 0.1 microns.

5 The particle size distribution of the powder coating composition may be in the range of from 0 to 120 microns, with a mean particle size in the range of from 15 to 75 microns, preferably 25-50 microns, more especially 20 to 45 microns.

10 In the case of relatively fine size distributions, especially where relatively thin applied films are required, for example, the powder coating composition may be one in which one or more of the following criteria is satisfied:

- 15 a) 95-100% by volume < 50 µm
- b) 90-100% by volume < 40 µm
- c) 45-100% by volume < 20 µm
- d) 5-100% by volume < 10 µm  
preferably 10-70% by volume < 10 µm
- 20 e) 1-80% by volume < 5 µm  
preferably 3-40% by volume < 5 µm
- f)  $d(v)_{50}$  in the range 1.3-32 µm  
preferably 8-24 µm

Powder coating compositions generally comprise a solid film-forming resin, usually with one or more colouring agents such as pigments, and optionally also contain one or more performance additives.

25 A powder coating composition for use according to the invention will in general be a thermosetting system (incorporating, for example, a film-forming polymer and a corresponding curing agent which may itself be another film-forming polymer), but thermoplastic systems (based, for example, on polyamides) can in principle be used instead.

35 The film-forming polymer used in the manufacture of a thermosetting powder coating composition for use

according to the invention may be one or more selected from carboxy-functional polyester resins, hydroxy-functional polyester resins, epoxy resins, and functional acrylic resins.

5       The composition may, for example, be based on a solid polymeric binder system comprising a carboxy-functional polyester film-forming resin used with a polyepoxide curing agent. Such carboxy-functional polyester systems are currently the most widely used  
10      powder coatings materials. The polyester generally has an acid value in the range 10-100, a number average molecular weight Mn of 1,500 to 10,000 and a glass transition temperature Tg of from 30°C to 85°C, preferably at least 40°C. The polyepoxide can, for  
15      example, be a low molecular weight epoxy compound such as triglycidyl isocyanurate (TGIC), a compound such as diglycidyl terephthalate or diglycidyl isophthalate, an epoxy resin such as a condensed glycidyl ether of bisphenol A or a light-stable epoxy resin. Such a  
20      carboxyfunctional polyester film-forming resin can alternatively be used with a bis(beta-hydroxy-alkylamide) curing agent such as tetrakis(2-hydroxyethyl) adipamide.

25      Alternatively, a hydroxy-functional polyester can be used with a blocked isocyanate-functional curing agent or an amine-formaldehyde condensate such as, for example, a melamine resin, a urea-formaldehyde resin, or a glycol ural formaldehyde resin, for example, the material "Powderlink 1174" supplied by the Cyanamid Company, or  
30      hexahydroxymethyl melamine. A blocked isocyanate curing agent for a hydroxy-functional polyester may, for example, be internally blocked, such as the urethane dione type, or may be of the caprolactam-blocked type, for example, isopherone diisocyanate.

35      As a further possibility, an epoxy resin can be used with an amine-functional curing agent such as, for example, dicyandiamide. Instead of an amine-functional

curing agent for an epoxy resin, a phenolic material may be used, preferably a material formed by reaction of epichlorohydrin with an excess of bisphenol A (that is to say, a polyphenol made by adducting bisphenol A and an 5 epoxy resin). A functional acrylic resin, for example a carboxy-, hydroxy- or epoxy-functional resin can be used with an appropriate curing agent. Mixtures of binders can be used, for example a carboxy-functional polyester can be used with a carboxy-functional acrylic resin and a 10 curing agent such as a bis(betahydroxyalkylamide) which serves to cure both polymers. As further possibilities, for mixed binder systems, a carboxy-, hydroxy- or epoxy-functional acrylic resin may be used with an epoxy resin or a polyester resin (carboxy- or hydroxy-functional). 15 Such resin combinations may be selected so as to be co-curing, for example, a carboxy-functional acrylic resin co-cured with an epoxy resin, or a carboxy-functional polyester co-cured with a glycidyl-functional acrylic resin. More usually, however, such mixed binder 20 systems are formulated so as to be cured with a single curing agent (for example, use of a blocked isocyanate to cure a hydroxy-functional acrylic resin and a hydroxy-functional polyester). Another preferred formulation involves the use of a different curing agent for each 25 binder of a mixture of two polymeric binders (for example, an amine-cured epoxy resin used in conjunction with a blocked isocyanate-cured hydroxy functional acrylic resin).

Other film-forming polymers which may be mentioned 30 include functional fluoropolymers, functional fluorochloropolymers and functional fluoroacrylic polymers, each of which may be hydroxy-functional or carboxy-functional, and may be used as the sole film-forming polymer or in conjunction with one or more 35 functional acrylic, polyester and/or epoxy resins, with appropriate curing agents for the functional polymers.

Other curing agents which may be mentioned include

- 13 -

epoxy phenol novolacs and epoxy cresol novolacs; isocyanate curing agents blocked with oximes, such as isopherone diisocyanate blocked with methyl ethyl ketoxime, tetramethylene xylene diisocyanate blocked with 5 acetone oxime, and Desmodur W (dicyclohexylmethane diisocyanate curing agent) blocked with methyl ethyl ketoxime; light-stable epoxy resins such as "Santolink LSE 120" supplied by Monsanto; and alicyclic poly-epoxides such as "EHPE-3150" supplied by Daicel.

10 The following ranges should be mentioned for the total film-forming resin content of a powder coating composition according to the invention (including curing agent, where appropriate, but disregarding dry blend additives):

15 40% to 100% by weight,  
47% to 100% by weight,  
47% to 90% by weight,  
53% to 99% by weight, and  
53% to 74% by weight.

20 As already explained, there may be more than one film-forming resin binder and curing agent, as appropriate.

A powder coating composition for use according to the invention may be free from added colouring agents, 25 but usually contains one or more such agents (pigments or dyes). Examples of pigments which can be used are inorganic pigments such as titanium dioxide, red and yellow iron oxides, chrome pigments and carbon black and organic pigments such as, for example, phthalocyanine, 30 azo, anthraquinone, thioindigo, isodibenzanthrone, triphendioxane and quinacridone pigments, vat dye pigments and lakes of acid, basic and mordant dyestuffs. Dyes can be used instead of or as well as pigments.

The composition of the invention may also include 35 one or more extenders or fillers, which may be used inter alia to assist opacity, whilst minimising costs, or more generally as a diluent.

The following ranges should be mentioned for the total pigment/filler/extender content of a powder coating composition according to the invention (disregarding dry blend additives) :

- 5        0% to 55% by weight,  
          0% to 50% by weight,  
          10% to 50% by weight,  
          0% to 45% by weight, and  
          25% to 45% by weight
- 10      Of the total pigment/filler/extender content, a pigment content of  $\leq$  40% by weight of the total composition (disregarding dry blend additives) may be used. Usually a pigment content of 25-30% is used, although in the case of dark colours opacity can be obtained with < 10% by weight of pigment.

The composition of the invention may also include one or more performance additives, for example, a flow-promoting agent, a plasticiser, a stabiliser against UV degradation, or an anti-gassing agent, such as benzoin, 20 or two or more such additives may be used. The following ranges should be mentioned for the total performance additive content of a powder coating composition according to the invention (disregarding dry blend additives) :

- 25      0% to 5% by weight,  
          0% to 3% by weight, and  
          1% to 2% by weight.

In general, colouring agents, fillers/extenders and performance additives as described above will be 30 incorporated before and/or during the extrusion or other homogenisation process, and not by dry blending.

A powder coating composition according to the invention may in principle be applied to a substrate by any of the processes of powder coating technology, for 35 example, by electrostatic spray coating (corona-charging or tribo-charging); or by fluidised-bed or electrostatic fluidised-bed processes.

After application of the powder coating composition to a substrate, conversion of the resulting adherent particles into a continuous coating (including, where appropriate, curing of the applied composition) may be 5 effected by heat treatment and/or by radiant energy, notably infra-red, ultra-violet or electron beam radiation.

The powder is usually cured on the substrate by the application of heat (the process of stoving); the powder 10 particles melt and flow and a film is formed. The curing times and temperatures are interdependent in accordance with the composition formulation that is used, and the following typical ranges may be mentioned:

	<u>Temperature/°C</u>	<u>Time</u>
15	280 to 100*	10 s to 40 min
	250 to 150	15 s to 30 min
	220 to 160	5 min to 20 min

\* Temperatures down to 90°C may be used for some resins, especially certain epoxy resins.

20 The substrate may comprise a metal, a heat-stable plastics material, wood, glass, or a ceramic or textile material. Advantageously, a metal substrate is chemically or mechanically cleaned prior to application of the composition, and is preferably subjected to chemical pre-treatment, for example, with iron phosphate, zinc 25 phosphate or chromate. Substrates other than metallic are in general preheated prior to application or, in the case of electrostatic spray application, are pretreated with a material that will aid such application.

30 Used as a single-component additive, wax-coated silica offers the possibility of eliminating or at least reducing the electrostatic interactions between the powder coating particles and between the powder particles and the tubing used for transport of powder coating 35 compositions to the application equipment. This in turn offers the possibility of achieving improved fluidity properties, with the further inherent practical advantage

- 16 -

of avoiding the additional manufacturing procedures, quality control measures, and costs involved in utilising a multi-component dry-blended additive.

The use of the wax-coated silica in the ternary  
5 additive of the invention offers the possibility of increasing the benefits, especially in terms of fluidity, provided by the previously proposed aluminium oxide/aluminium hydroxide combination alone. In particular, for example, the use of the wax-coated silica in tribo-charging systems offers the possibility of using aluminium oxide-rich additive blends to promote tribo-charging without detracting from the good fluidity, transport and handling properties attributable to the aluminium additive combination.

In general, the use of one or more additives in accordance with the invention offers an improvement in the first-time deposition of fine particles (especially particles of 10 microns or less) which in turn leads to improved uniformity of film weight on the substrate (and hence to a reduction in the amount of powder needed to achieve a given nominal film weight) and to reduced accumulation of fine particles in the recycling system.

The improved first-time deposition of fine powder coating particles that can be achieved in accordance with the invention also has the advantageous consequence of enabling a higher proportion of such particles to be accommodated in powder coating compositions without undue deleterious effects. In principle, this in turn contributes to improved film appearance and tends to facilitate the production of thin films.

The invention is applicable over a wide range of film thicknesses, typically from thin films of, for example, 30 microns or less up to films of 100 to 150 microns.

35

#### EXAMPLES

The following Examples illustrate the invention:-

- 17 -

The aluminium oxide used in the Examples was Aluminium Oxide C, ex Degussa, mean particle size < 0.2 microns; the aluminium hydroxide used was Martinal OL 103C, ex Omya Croxton & Garry, mean particle size 5 0.8 microns; and the silica used was Gasil 937, ex Crosfield, mean particle size 6.5 microns (a micronised silica gel coated with microcrystalline paraffin wax).

10 The dry-blend additive compositions used in the Examples were prepared as follows:-

Dry-blend Additive Composition 1

	Aluminium oxide	7.2 parts by weight
15	Aluminium hydroxide	8.8 parts by weight
	Silica	4.0 parts by weight

The additive materials were charged to a Moulinex II high-shear blender, mixed for 30 seconds and allowed to cool. The mixing and cooling process was repeated twice 20 to give a total of three operations. The resulting mixed additive was reserved for future use.

Dry-blend Additive Composition 2

	Aluminium oxide	5.4 parts by weight
25	Aluminium hydroxide	6.6 parts by weight
	Silica	8.0 parts by weight

The additive materials were charged to a Moulinex II high-shear blender, mixed for 30 seconds and allowed to cool. The mixing and cooling process was repeated twice 30 to give a total of three operations. The resulting mixed additive was reserved for future use.

Dry-blend Additive Composition 3

	Aluminium oxide	10 parts by weight
35	Silica	10 parts by weight

The additive materials were charged to a Moulinex II high-shear blender, mixed for 30 seconds and allowed to

- 18 -

cool. The mixing and cooling process was repeated twice to give a total of three operations. The resulting mixed additive was reserved for future use.

5    Dry-blend Additive Composition 4

Aluminium hydroxide	7 parts by weight
Silica	13 parts by weight

The additive materials were charged to a Moulinex II high-shear blender, mixed for 30 seconds and allowed to cool. The mixing and cooling process was repeated twice to give a total of three operations. The resulting mixed additive was reserved for future use.

15    Dry-blend Additive Composition 5

Silica

The additive material was used as supplied.

20    Dry-blend Additive Composition 6

Aluminium oxide	12.8 parts by weight
Aluminium hydroxide	3.2 parts by weight
Silica	4 parts by weight

The additive materials were charged to a Moulinex II high-shear blender, mixed for 30 seconds and allowed to cool. The mixing and cooling process was repeated twice to give a total of three operations. The resulting mixed additive was reserved for future use.

25    Dry-blend additive composition 7

Aluminium oxide	6.7 parts by weight
Aluminium hydroxide	6.7 parts by weight
Silica	6.7 parts by weight

The additive materials were charged into a Moulinex II high-shear blender, mixed for 30 seconds and allowed to cool. The mixing and cooling process was repeated twice to give a total of three operations. The resulting mixed additive was reserved for future use.

The particle size distribution data reported in the Examples was obtained using the equipment indicated in each case (Coulter Counter Multisizer II or the Mastersizer X laser light-scattering device from Malvern Instruments). The data is expressed partly in volume percentiles  $d(v)_x$ , where X is the percentage of the total volume of the particles that lies below the stated particle size d. Thus, for instance,  $d(v)_{50}$  is the median particle size of the sample.

10

Example 1:White matt polyester powder coating composition  
- deposited film weight tests

The composition of Example 1 was prepared from two components as follows:

	<u>% by weight</u>
Component A	
Carboxy-functional polyester polymer	
Acid Value 77	26.40
Primid XL552 (EMS Grilon)	2.80
Benzoin	0.15
Flow agent	0.40
PTFE modified polyethylene wax	1.00
Polyolefin material (matting agent)	
- Grilonit 68022 (EMS Grilon)	0.20
Rutile titanium dioxide	17.00
Extender	2.00

	<u>% by weight</u>
Component B	
Carboxy-functional polyester	
polymer with Acid Value 29	23.70
Primid XL552 (EMS Grilon)	0.75
Benzoin	0.15
Flow agent	0.40
PTFE modified polyethylene wax	1.00
Polyolefin material (matting agent)	
- Grilonit 68022 (EMS Grilon)	0.25
Rutile titanium dioxide	17.00

- 20 -

Extender	2.00
Hydroxy-functional polyester polymer with Hydroxyl Value 45	4.80
	<hr/>
5	Total 100.00

The ingredients for Component A were dry mixed in a blender, and fed into a twin-screw extruder operating at a temperature of 108°C. The extrudate was rolled flat on a chilled plate and broken into chip form (ca. 1 cm mesh). The ingredients for Component B were likewise dry mixed in a blender, and fed into a twin-screw extruder operating at a temperature of 108°C. The extrudate was rolled flat on a chilled plate and broken into chip form (ca. 1 cm mesh). The two Components thereby obtained in chip form were thoroughly mixed in equal weight ratios and then ground in an impact mill to produce a powder coating composition I having the following particle size distribution (determined using a Coulter Counter Multisizer II):

d(v) <sub>99</sub>	< 115 microns
d(v) <sub>50</sub>	45 microns
5.2%	< 10 microns
1.6%	< 5 microns

A part of the powder coating composition I was then dry blended with a 0.4% by weight addition of additive composition 1 [(aluminium oxide/aluminium hydroxide/wax-coated silica (20% of total additive by weight)]. The resulting composition was then electrostatically spray applied to perforated steel ceiling tiles (585 mm wide x 585 mm high x 0.5 mm thick, each tile being perforated by a grid of 101 x 101 holes of approximately 2 mm diameter and 4 mm separation) using an ITW Gema Volstatic corona application gun (gun settings: fluidising air 1.0 bar, conveying air 0.6 bar, supplementary air 3 m<sup>3</sup> hour<sup>-1</sup>, single corona needle conical baffle nozzle at 70 kV) and reciprocator (reciprocator settings: speed 0.35 m s<sup>-1</sup> in

- 21 -

both vertical directions, traverse 66 cm about the centre of the ceiling tile). The ceiling tiles were introduced to the application booth by means of a moving track (track speed: 1.22 m min<sup>-1</sup>). The applied powder coatings 5 were stoved to give cured films of 70.5 microns average film thickness, (stoving conditions: 15 minutes at 180°C).

A further part of the powder coating composition I was then dry blended with a 0.4% by weight addition of 10 additive composition 2 [aluminium oxide/aluminium hydroxide/wax-coated silica (40% of total additive by weight)]. This was applied and stoved under the same conditions as above to give cured films of 73.5 microns average film thickness.

15 In order to provide a basis for comparison with Example 1, a further part of the powder coating composition I was dry blended with a 0.1% by weight addition of an uncoated pyrogenic silica (Acematt TS 100 ex Degussa). Application and stoving of the resulting 20 composition under the same conditions as Example 1 gave cured films of average film thickness 39.0 microns on the steel ceiling tiles.

The greater film weight obtained when using additive compositions in accordance with the invention offers the 25 possibility of increasing the rate of passage of substrate articles through the spray-coating booth, with resulting productivity gains, and/or reducing the air pressure used to transport powder through the application system, leading to reduced equipment wear. Also, it may 30 be noted that increasing the proportion of wax-coated silica in the additive (from 20% by weight in additive composition 1 to 40% by weight in additive composition 2) did not significantly affect the film weight deposited under the described application and stoving conditions.

- 22 -

Example 2:

White matt polyester powder coating composition

- transfer efficiency test

A quantity of the powder composition I from Example 1 was dry-blended with a 0.4% by weight addition of additive composition 1 [aluminium oxide/aluminium hydroxide/wax-coated silica (20% of total additive by weight)]. The resulting composition was then applied to a single fixed panel (dimensions: height 61 cm, width 40 cm) using an ITW Gema Volstatic powder coating application unit (gun settings: fluidising air 1.0 bar, conveying air 0.6 bar, supplementary air  $3 \text{ m}^3 \text{ hour}^{-1}$ , single corona needle conical baffle nozzle at 70 kV centred on the panel at a distance of 29 cm distant) for 10 seconds. The weight of powder adhering to the panel was measured. The weight of powder lost from the fluidised-bed powder reservoir during application was measured. The transfer efficiency was calculated according to the following Equation I (static test):

20

Equation I:

$$\text{Transfer Efficiency} = \frac{M_{\text{Panel}}(t)}{M_F(t)} \times 100\%$$

where:

25

$M_{\text{Panel}}(t)$  = mass of powder coating on the panel after application time  $t$ .

30

$M_F(t)$  = mass of powder lost from the fluidised-bed reservoir after application time  $t$ .

The panel was cleaned, and the transfer efficiency test repeated for 20 seconds application time and 30 seconds application time.

35

A further quantity of the powder coating composition I was then dry blended with a 0.4% by weight

- 23 -

addition of additive composition 2 [aluminium oxide/aluminium hydroxide/wax-coated silica (40% of total additive by weight)]. The 10-, 20-, and 30-second transfer efficiencies of the resulting composition were  
5 measured as described above.

In order to provide a basis for comparison with Example 2, the application and testing procedure was repeated using a further quantity of the powder coating composition I, this time dry blended with a 0.1% by  
10 weight addition of the uncoated pyrogenic silica additive TS 100 as used in Example 1.

The results obtained are summarised in Table 1 below (in each case the summary figure representing the average of a series of experiments):

15

Table 1

Additive	Transfer Efficiency (%)		
	10 s	20 s	30 s
Comparison (TS100)	76	74	74
Additive Composition 1	74	71	71
Additive Composition 2	72	69	68

Considering the transfer efficiency data summarised  
20 above in conjunction with the deposition data from Example 1, it can be seen that the greatly increased throughput shown in Example 1 can more than compensate for the slightly reduced transfer efficiency shown in Example 2 when using an additive comprising a wax-coated  
25 silica in accordance with the present invention. This offers the possibility of achieving the beneficial effects of aluminium oxide addition without adverse effects derived from reduced transfer efficiency.

In order to provide a further comparison between the

- 24 -

additive compositions according to the invention in Example 2 and the TS100 uncoated silica additive, the powder application procedure was repeated with adjustment of the conveying air pressure so as to obtain  
 5 approximately the same throughput (approximately 2 g sec<sup>-1</sup>) in each case. The conveying air pressure required for this purpose in the case of the TS 100 additive was 1.5 bar, whereas the required pressure was only 1.1 bar in the case of the additive compositions of  
 10 Example 2. The mass of powder coated onto the substrate panel per unit time was determined in each experiment, and Table 2 below gives the results in summary form (in each case the summary figure representing the average of a series of experiments at 10-, 20- and 30-second  
 15 application time).

Table 2

Additive	Mass coated per unit time at coating times shown		
	10 s	20 s	30 s
Comparison (TS 100)	1.88±0.39	1.41±0.01	1.46±0.03
Additive Composition 1	1.63±0.13	1.59±0.09	1.51±0.04
Additive Composition 2	1.63±0.10	1.45±0.01	1.46±0.06

20 It will be seen that the mass coated per unit time shows little or no significant difference between the TS 100 additive and the additive compositions of the invention. At the same time, however, the conveying air pressure required to maintain throughput constant at  
 25 approximately 2 g s<sup>-1</sup> was significantly lower in the case of the additive compositions of the invention, which in turn means less wear on the application equipment whilst obtaining comparable results in other respects.

Example 3White semi-gloss polyester powder coating composition  
- performance testing

5 The composition of Example 3 was prepared as follows:

	<u>% by weight</u>
Carboxy-functional polyester	
polymer with Acid Value 29	51.90
10 Primid XL 552 (EMS Grilon)	1.90
Flow agent	0.80
Polyethylene wax	0.20
Benzoin	0.20
Rutile titanium dioxide	30.00
15 Extender	15.00
Total	100.00

20 The ingredients were dry mixed in a blender and fed into a twin-screw extruder operating at 108°C. The extrudate was rolled flat on a chilled plate and broken into chip form.

25 Two batches of milled powder were prepared from the resulting chip: one batch incorporating by dry blending a 0.5% by weight addition of additive composition 1 in accordance with the invention, and the other incorporating by dry blending - as a basis for comparison - a 0.1% by weight addition of aluminium oxide. Additive composition 1 [aluminium oxide/aluminium hydroxide/wax-coated silica (20% of total additive by weight)] was incorporated by volumetric feed injection into the mill. The aluminium oxide was incorporated by blending into the chip prior to milling.

30 In each case the milling was carried out in an impact mill (Hosokawa Micron ACM 5) to produce a composition having the following particle size distribution (determined using a Malvern Mastersizer X):-

- 26 -

$d(v)_{99}$	< 106 microns
$d(v)_{50}$	42 microns
7.5%	< 10 microns

- As a basis for comparison, the powder incorporating  
 5 the aluminium oxide additive was applied by electrostatic spray to a series of steel garage doors comprising light gauge panels surrounded by a heavy gauge frame. The light gauge panels were formed with a series of transverse recesses each 0.5 cm deep and 0.5 cm wide.
- 10 The powder coating composition was applied using Nordson VersaSpray II electrostatic spray guns, with 18 guns coating the front surface of the doors and 10 guns coating the rear surface of the doors. The garage doors were introduced into the application booth by means of a moving track (track speed: 5 m min<sup>-1</sup>). The applied powder coatings were stoved to give cured films (stoving conditions of half electric IR, half electric convection oven, with total time in oven 6.5 minutes).
- 15

The gun settings used were as follows:

20

Gun Number	Powder Air/psi	Diluting Air/psi	Gun Voltage/kv
1 (front)	24	24	100
2 (front)	26	27	100
3 (front)	28	28	100
4 (front)	28	28	100
5 (front)	32	26	100
6 (front)	34	30	100
7 (front)	26	27	100
8 (front)	24	28	100
9 (front)	28	28	100
10 (front)	24	26	100
11 (front)	24	26	100
12 (front)	26	24	100
13 (front)	26	26	100
14 (front)	30	30	100

15 (front)	25	24	100
16 (front)	22	24	100
17 (front)	24	26	100
18 (front)	28	26	100
19 (back)	20	22	100
20 (back)	22	28	100
21 (back)	20	22	100
22 (back)	30	30	100
23 (back)	26	26	100
24 (back)	27	28	100
25 (back)	20	24	100
26 (back)	24	29	100
27 (back)	24	30	100
28 (back)	30	26	100

Using these conditions the average coating weight per garage door was 822 g, with a standard deviation of 29 g (based upon coating 16 garage doors). The

5 penetration of the powder coating into the recessed areas was visually assessed as inadequate; substrate could be seen through the coating. The average film thickness on the heavy gauge supporting frame was 66 microns with a standard deviation of 22 microns (based upon 32 measurements over two garage doors). The average film thickness on the light gauge door surface was 53 microns with a standard deviation of 8 microns (based upon 24 measurements over two garage doors).

The powder coating composition incorporating  
15 additive composition 1 in accordance with the invention, was electrostatically spray applied to garage doors using exactly the same gun and booth conditions as above. The applied powder coatings were stoved to give cured films (stoving conditions of half electric IR, half electric convection oven, with total time in oven 6.5 minutes).

Using these conditions the average coating weight per garage door was 751 g, with a standard deviation of

59 g (based upon coating 18 garage doors). The penetration of the powder coating into recessed areas was visually assessed as superior to the comparison formulation, despite the lower average coating weight per 5 garage door. The average film thickness on the heavy gauge supporting frame was 57 microns with a standard deviation of 20 microns (based upon 48 measurements over three garage doors). The average film thickness on the light gauge door surface was 49 microns with a standard deviation of 10 microns (based upon 36 measurements over 10 three garage doors).

Example 4

White gloss polyester powder coating composition

15 The composition of Example 4 was prepared as follows:

% by weight

Carboxy-functional polyester polymer	
Acid value 40	50.08
TGIC PT810 (Ciba-Geigy)	3.77
20    Benzoin	0.15
PTFE modified polyethylene wax	1.00
Flow agent	0.80
Rutile titanium dioxide	30.00
Extender	14.20
25	
	Total
	100.00

The ingredients were dry mixed in a blender and fed into a twin-screw extruder operating at 105°C. The 30 extrudate was rolled flat on a chilled plate and broken into chip form.

Three batches of milled powder were prepared from the resulting chip: one batch incorporating by dry blending a 0.4% by weight addition of additive 35 composition 3 in accordance with the invention [aluminium oxide/wax-coated silica], one batch incorporating by dry blending a 0.4% by weight addition of additive

- 29 -

composition 4 [aluminium hydroxide/wax-coated silica], and one batch incorporating by dry blending a 0.4% by weight addition of additive composition 5 [wax-coated silica alone].

5 In each case the milling was carried out in an impact mill (Hosokawa ACM5) to produce a composition having the following particle size distribution (Malvern Mastersizer X) :-

	d(v) <sub>99</sub>	< 97
10	d(v) <sub>50</sub>	37
	8.5 %	< 10 microns

The resulting powder coating compositions were spray applied to flat aluminium panels (0.8 m x 0.8 m) using an ITW Gema Volastatic corona application gun (gun settings: 15 fluidising air 1.0 bar, conveying air 0.6 bar, supplementary air 3.5 m<sup>3</sup> hour<sup>-1</sup>, single corona needle conical baffle nozzle at 50 kV) and reciprocator (reciprocator settings: speed 0.35 m s<sup>-1</sup> in both vertical directions, traverse of 90 cm about the centre of the 20 aluminium panel). The panels were introduced to the application booth by means of a moving track (track speed: 0.98 m min<sup>-1</sup>). The moving panel transfer efficiency was according to the following Equation II (moving-panel test):

25

Equation II:

$$\text{Transfer Efficiency} = \frac{M_{\text{Panel}}}{\text{Throughput} \times [\text{Panel length/track speed}]} \times 100\%$$

where:

30 M<sub>Panel</sub> = mass of powder coating on the panel after one pass across the application gun.

Throughput = mass of powder lost from the fluidised-bed reservoir during application (g s<sup>-1</sup>)

The panel length divided by the track speed gives 35 the total time that the panel is in front of the application gun.

- 30 -

The results cited in Table 3 below are the average of three experiments. In addition a ceiling tile (as described in Example 1) was coated using these application conditions. The coated ceiling tile was 5 stoved to give cured films (stoving conditions: 15 minutes at 180°C).

Table 3

Powder coating containing additive composition	Transfer efficiency data (%) *	Stoved ceiling tile film thickness ( $\mu\text{m}$ ) *
3	56.3 $\pm$ 2.0	36 $\pm$ 9
4	57.8 $\pm$ 3.1	61 $\pm$ 16
5	52.5 $\pm$ 1.8	53 $\pm$ 17

10

\*  $\pm$  figures denote 1 standard deviation in data.

It will be seen that there is no significant difference between the transfer efficiencies achieved 15 using the three different additive compositions of the invention; all of the values achieved are considered acceptable. At the constant application pressure employed in the experiments the applied film thickness achieved with composition 3 (aluminium oxide/wax-coated silica) 20 was relatively low, but the throughput was also relatively low, reflecting the different fluidising efficiency of composition 3. A greater film thickness could in principle have been achieved by increasing the air pressure to achieve a higher throughput.

25

#### Example 5

##### Study of deposition of fines/Transfer efficiency

##### White gloss polyester-epoxy hybrid powder coating

##### composition

30 The composition of Example 5 was prepared as follows:

	<u>% by weight</u>
Carboxy-functional polyester polymer	
Acid value 55	32.31
Type 2 epoxy resin (GT7072, ex Ciba-Geigy)	21.54
5    Benzoin	0.15
PTFE modified polyethylene wax	1.00
Flow agent	0.80
Rutile titanium dioxide	40.00
Extender	4.20
10	
	Total
	100.00

The ingredients were dry mixed in a blender and fed into a twin-screw extruder operating at 90°C. The 15 extrudate was rolled flat on a chilled plate and broken into chip form.

Two batches of milled powder were prepared from the resulting chip: one batch incorporating by dry blending a 0.4% by weight addition of additive composition 6 in 20 accordance with the invention, and one batch incorporating by dry blending, in order to provide a basis for comparison, a 0.4% by weight addition of an additive composition comprising 80% by weight of aluminium oxide and 20% by weight of aluminium hydroxide.

25 In each case the milling was carried out in an impact mill (Hosokawa ACM5) to produce a composition having the following particle size distribution (Malvern Mastersizer X) :-

	$d(v)_{99}$	< 55
30	$d(v)_{50}$	21
	12.0%	< 10 microns

The resulting powder coating compositions were spray applied to flat aluminium panels (0.8 m x 0.8 m) using a Nordson type II tribostatic application gun (gun 35 settings: fluidising air 1 bar, conveying air 4 bar, supplementary air 4 bar, eight finger diffuser nozzle attachment) and reciprocator (reciprocator settings:

upper limit "1.6", lower limit "5.4", speed in both directions "6"). The panels were introduced to the application booth by means of a moving track (track speed:  $2.6 \text{ m min}^{-1}$ ). The moving panel transfer efficiency 5 was calculated as described in Example 4. The results cited in Table 4 below are the average of three experiments.

Without curing, samples of applied powder coating were removed from the panels and the particle size 10 distribution of the applied powder was measured by means of a Malvern Mastersizer X.

Table 4

Powder containing additive composition	6	Comparison
$d_{(v)99}$	55 microns	51
$d_{(v)50}$	28 microns	25
Percentage below 10 microns	7	4
Transfer Efficiency	61%*	49%**

15

\* Standard deviation: 7.5%

\*\*Standard deviation: 7%

It will be seen that the transfer efficiency 20 achieved using the ternary additive composition 6 according to the invention (aluminium oxide/aluminium hydroxide/wax-coated silica, with a 4:1 ratio of aluminium oxide to aluminium hydroxide) was significantly better than that achieved in the comparison experiment 25 (aluminium oxide/aluminium hydroxide additive, also 4:1, but no wax-coated silica).

It will also be seen that, to a simple 30 approximation, the proportion of the sub-10 micron fines fraction deposited on the substrate was much greater for the powder incorporating the additive composition according to the invention than for the powder

incorporating the comparison additive. This result offers various advantages as discussed hereinbefore.

Example 6

5        Seven batches of milled powder were prepared from powder coating composition chip prepared as described in Example 5. Four of the batches incorporated, by dry blending, 0.4% by weight additions of additive compositions 3, 4, 5 and 7 in accordance with the  
10      invention. In order to provide a basis for comparison, the remaining three batches incorporated, by dry blending, 0.4% by weight additions of aluminium oxide, aluminium hydroxide and an aluminium oxide/aluminium hydroxide mixture comprising 50% by weight of each  
15      component and prepared as described for the mixed additive compositions of the invention.

In each case the milling was carried out in an impact mill (Alpine laboratory will) to produce a composition having the following particle size  
20      distribution (Malvern Mastersizer X) :

$d(v)_{99}$	< 57
$d(v)_{50}$	22
18%	< 10 microns

The transfer efficiency of the resulting powder  
25      coating compositions was assessed by a parallel plate test. An arrangement of two metal plates (each 1 m x 1 m) separated by 30 cm was used in a non-extracted booth housed in a conventional powder spray booth. Prior to carrying out the transfer efficiency test, the  
30      application air pressure was adjusted to obtain a throughput of  $4.1 \pm 0.6 \text{ g s}^{-1}$  (fluidising air pressure 1.5-2.0 bar to achieve the desired throughput, conveying air 2.5 bar, supplementary air 1.8 bar).

The powder was sprayed using a Nordson Type II tribo  
35      gun with the Nordson eight-finger diffuser attachment. Powder was sprayed for 20 seconds into the booth. The wieght of powder adhering to the parallel plates was

measured, as was the weight of coating lost from the fluidised bed during spraying. The ratio of these two weights was used to calculate the transfer efficiency in each case, as described in example 2. Tests were 5 repeated three times for each powder coating sample.

Without curing, samples of applied powder coating were removed from the panels and the particle size distribution of the applied powder was measured by means of a Malvern Mastersizer X. The resulting data was used 10 to calculate the percentage of sub-10 micron fine particles deposited in each case.

The deposition efficiency and % fines deposited data are summarised in the following Table 5:

15 Table 5

Additive	Transfer Efficiency	% Fines deposited
Composition 3 [Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> ]	71.9 ± 3.7%	100%
Composition 4 [Al(OH) <sub>3</sub> /SiO <sub>2</sub> ]	74.7%	94.5%
Composition 5 [SiO <sub>2</sub> ]	70.7 ± 2.0%	98.6 ± 0.3%
Composition 7 [Al <sub>2</sub> O <sub>3</sub> /Al(OH) <sub>3</sub> /SiO <sub>2</sub> ]	78.9 ± 1.5%	92.3 ± 1.8%
Comparison [Al <sub>2</sub> O <sub>3</sub> ]	68.9 ± 0.7%	88.9 ± 2.6%
Comparison [Al(OH) <sub>3</sub> ]	70.4 ± 3.2%	93.4 ± 2.2%
Comparison [Al <sub>2</sub> O <sub>3</sub> /Al(OH) <sub>3</sub> ]	68.9 ± 1.3%	95.0 ± 0.8%

Taking into account both transfer efficiency and fines deposition, the results achieved using the 20 additives according to the invention were superior to those achieved using the various comparison additives.

- 35 -

In addition, the best results in terms of transfer efficiency were achieved using the ternary additive of the invention, and the best results in terms of fines deposition were achieved using the aluminium oxide/waxed silica additive of the invention, whilst the waxed silica sole additive of the invention give results which were almost as good.

CLAIMS

1. A powder coating composition which incorporates, by dry blending, a wax-coated silica additive in finely divided form.
- 5 2. A powder coating composition as claimed in claim 1, wherein the silica comprises a precipitated silica or a silica gel.
- 10 3. A powder coating composition as claimed in claim 1 or claim 2, wherein the wax comprises an animal wax, a vegetable wax, a petroleum wax or a synthetic wax.
- 15 4. A powder coating composition as claimed in claim 3, wherein the wax comprises a microcrystalline wax.
- 20 5. A powder coating composition as claimed in claim 1 or claim 2, wherein the wax comprises an ester of an aliphatic alcohol having at least 16 carbon atoms with a fatty acid having at least 16 carbon atoms.
- 25 6. A powder coating composition as claimed in claim 1 or claim 2, wherein the wax comprises a salt of a fatty acid having at least 16 carbon atoms.
- 30 7. A powder coating composition as claimed in claim 6, wherein the wax comprises aluminium stearate.
- 35 8. A powder coating composition as claimed in any one of claims 1 to 7, wherein the amount of wax coated onto the silica is in the range of from 2 to 10% by weight.
9. A powder coating composition as claimed in any one of claims 1 to 8, wherein the amount of wax-coated silica additive is in the range of from 0.002 to 2.0% by weight, based on the total weight of the composition without the additive, advantageously from 0.02 to 1.5% by weight, preferably from 0.04 to 1.0% by weight, more especially at least 0.2% by weight, especially 0.3 to 0.7% by weight.
- 35 10. A powder coating composition as claimed in any one of claims 1 to 8 which also incorporates as additive(s), by dry blending, aluminium oxide, aluminium

hydroxide or aluminium oxide and aluminium hydroxide.

11. A powder coating composition as claimed in claim 10, wherein the total content of additives incorporated by dry blending is in the range of from 0.1 to 5% by weight, based on the total weight of the composition without the additives, advantageously from 0.1 to 2% by weight, preferably at least 0.2% by weight, especially from 0.2 to 1.5% by weight, more especially 0.3 to 1% by weight.

10 12. A powder coating composition as claimed in claim 10 or claim 11 which incorporates, by dry blending, wax-coated silica and aluminium oxide in relative proportions by weight of from 99:1 to 1:99, advantageously from 80:20 to 20:80, preferably from 70:30

15 to 30:70.

13. A powder coating composition as claimed in claim 10 or claim 11 which incorporates, by dry-blending, wax-coated silica and aluminium hydroxide in relative proportions by weight of from 99:1 to 30:70, advantageously from 90:10 to 40:60, preferably from 80:20 to 50:50.

14. A powder coating composition as claimed in claim 10 or claim 11 which incorporates, by dry blending, wax-coated silica, aluminium oxide and aluminium hydroxide in relative proportions by weight as follows:

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Al(OH) <sub>3</sub>
	1 to 98%	1 to 98%	1 to 70%
advantageously	5 to 50%	10 to 90%	1 to 60%
30 preferably	10 to 30%	20 to 85%	1 to 55%

15. A powder coating composition as claimed in any one of claims 1 to 14, wherein there is more than one additive incorporated by dry blending and the additives are pre-mixed before being incorporated in the 35 composition.

16. A powder coating composition as claimed in any one of claims 1 to 15, wherein the particle size of

the or each additive incorporated by dry blending is up to 10 microns, advantageously up to 5 microns, preferably up to 2 microns, and more especially up to 1 micron.

17. A powder coating composition as claimed in  
5 claim 16, wherein the particle size of the or each  
additive incorporated by dry blending is at least  
0.1 micron.

18. A powder coating composition as claimed in  
any one of claims 1 to 17, which is a thermosetting  
10 system.

19. A powder coating composition as claimed in  
claim 18, which incorporates a film-forming polymer  
selected from carboxy-functional polyester resins,  
hydroxy-functional polyester resins, epoxy resins, and  
15 functional acrylic resins.

20. A powder coating composition as claimed in  
any one of claims 1 to 19, wherein the particle size  
distribution of the composition is such that one or more  
of the following criteria is satisfied:

- 20           a) 95-100% by volume < 50 µm
- b) 90-100% by volume < 40 µm
- c) 45-100% by volume < 20 µm
- d) 5-100% by volume < 10 µm,  
                preferably 10-70% by volume < 10 µm
- 25           e) 1-80% by volume < 5 µm,  
                preferably 3-40% by volume < 5 µm
- f)  $d(v)_{50}$  in the range 1.3-32 µm,  
                preferably 8-24 µm,  $d(v)_{50}$  being the  
                particle size below which 50% by volume  
                of the particles in the composition is  
                found.

30           21. A process for forming a coating on a  
substrate, in which a composition as claimed in any one  
of claims 1 to 20 is applied to the substrate by a powder  
35           coating process resulting in particles of the composition  
adhering to the substrate, and forming the adherent  
                particles into a continuous coating over at least part of

- 39 -

the substrate.

22. A coated substrate obtained by a process as claimed in claim 21.

# INTERNATIONAL SEARCH REPORT

Internat'l Application No  
PCT/GB 99/02109

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 C09D5/03

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C09D C08K C09C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 311 527 A (NIPPON PAINT CO) 1 October 1997 (1997-10-01) abstract; claims ----	1,21,22
A	WO 97 08250 A (CROSFIELD LTD) 6 March 1997 (1997-03-06) ----	1
A	FR 1 585 800 A (DEGUSSA) 30 January 1970 (1970-01-30) & US 3 607 337 A cited in the application ----	1
A	US 3 816 154 A (HENRY BALDYGA) 11 June 1974 (1974-06-11) cited in the application ----	1
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

15 October 1999

28/10/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Girard, Y

**INTERNATIONAL SEARCH REPORT**

Internat'l Application No

PCT/GB 99/02109

**C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 004, no. 182 (C-035), 16 December 1980 (1980-12-16) & JP 55 123678 A (TOSHIBA CORP), 24 September 1980 (1980-09-24) abstract -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat'l Application No

PCT/GB 99/02109

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
GB 2311527	A 01-10-1997	JP 9255896 A		30-09-1997
		CN 1170019 A		14-01-1998
		DE 19712765 A		20-11-1997
-----				
WO 9708250	A 06-03-1997	AU 6736396 A		19-03-1997
		CA 2229262 A		06-03-1997
		EP 0861298 A		02-09-1998
-----				
FR 1585800	A 30-01-1970	DE 1592865 A		18-02-1971
		BE 722073 A		14-03-1969
		CH 531989 A		31-12-1972
		GB 1236775 A		23-06-1971
		NL 6814075 A,B,		15-04-1969
		US 3607337 A		11-05-1971
		DE 1667465 A		09-09-1971
		ES 358940 A		01-07-1971
-----				
US 3816154	A 11-06-1974	AR 200313 A		31-10-1974
		AU 6772074 A		16-10-1975
		CA 1016304 A		30-08-1977
		DE 2419759 A		05-12-1974
		GB 1461511 A		13-01-1977
		JP 50010819 A		04-02-1975
-----				
JP 55123678	A 24-09-1980	NONE		
-----				